

INFRARED SPECTRA OF MOLECULES AND MATERIALS
OF ASTROPHYSICAL INTEREST

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Introduction

Methylamine, CH_3NH_2 , is a compound that may occur in the atmospheres of the Jovian planets. This compound is of considerable spectroscopic interest because it contains both inversion and internal rotation. Lord and Gray¹ have carried out a very extensive infrared investigation of four isotopes of this compound in the gas phase using normal path lengths. Recently Crawford, et al.,² carried out a normal coordinate analysis of this molecule and its isotopic derivatives using the Urey-Bradley force field with a least squares adjustment of the force constants to fit the observed vibrational frequencies of all four available isotopic molecules. The only frequency which was uncertain in the assignment of Lord and Gray was the NH_2 twisting vibration, ν_{13} , of A'' species. Thus Crawford et al.,² gave zero weight to the twisting frequencies for all isotopes and compared this calculation to the observed frequencies. They² were able then to give a modified assignment of the NH_2 twisting frequencies as follows: CH_3NH_2 , 977 cm^{-1} ; CH_3ND_2 , 744 cm^{-1} ; CD_3NH_2 , 1078 cm^{-1} and CD_3ND_2 at 701 cm^{-1} based on the normal coordinate calculation.

Inspection of the recorded spectra of Lord and Gray¹ shows no bands in the regions predicted for three out of four compounds. But as was pointed out by Crawford et al.,² the twisting frequencies are known to be weak. Mann et al.,³ have shown the usefulness of studying stable compounds by the matrix isolation technique.⁴

They³ have shown the similarity of the gas phase spectrum to the matrix spectrum and how it is possible to eliminate difference bands. Thus, it was hoped that an investigation of the four isotopic species in the matrix at liquid hydrogen temperature could confirm or reject the normal coordinate assignments. It could also give a firm footing for assigning the NH_2 twisting frequencies in hydrazine and other primary amines.

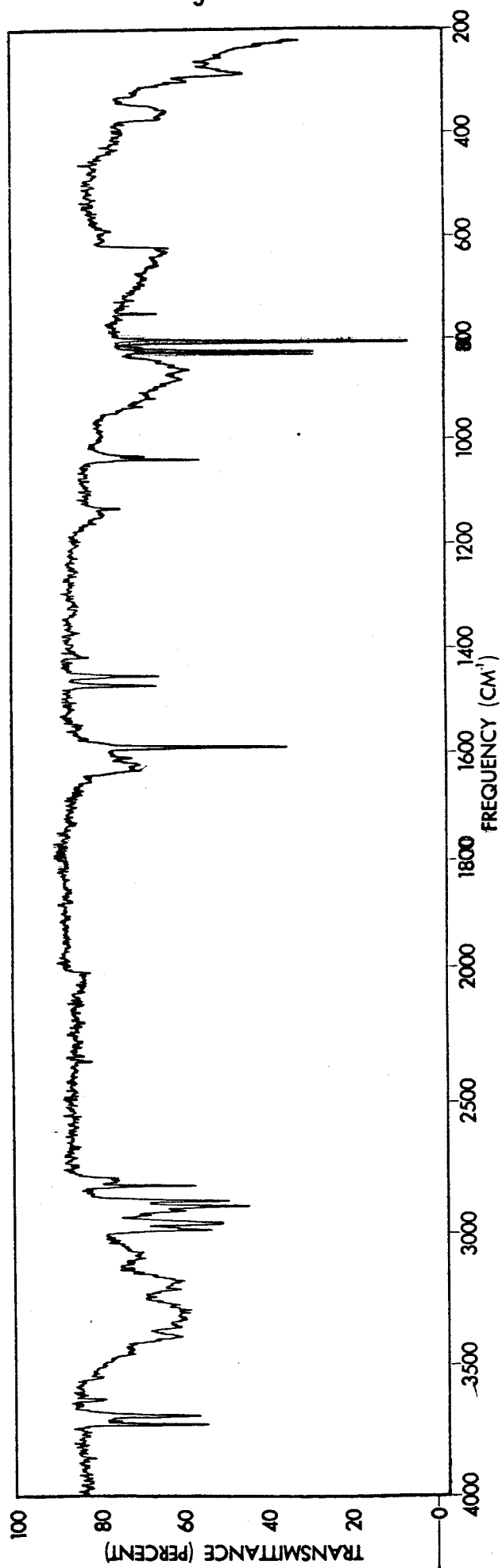
Vibrational Spectrum of Matrix Isolated CH_3NH_2

As a continuation of our studies on methylamine, most of our time thus far has been devoted to perfecting experimental conditions such as deposition rates, times, amounts and sampling techniques, etc. Also it seems to make a considerable amount of difference which matrix material is used for isolation. Of the two matrix materials (N_2 and Ar) thus far used, nitrogen gives better results with smaller band widths and sharper band centers. As an example of the relatively drastic changes encountered on changing the isolation matrix material, the two strongest bands in the spectrum of CH_3NH_2 in a 1:450 mole ratio with N_2 occur at 816 and 841 cm^{-1} with the higher frequency band being by far the weakest of the two. However, in the spectrum of CH_3NH_2 in a 1:450 mole ratio with Ar, these two bands occur at 790 and 797 cm^{-1} with the lower frequency band now being the weakest.

Our best spectra to date have been recorded using a deposition rate of 60 μM of matrix sample per minute. Other workers advise

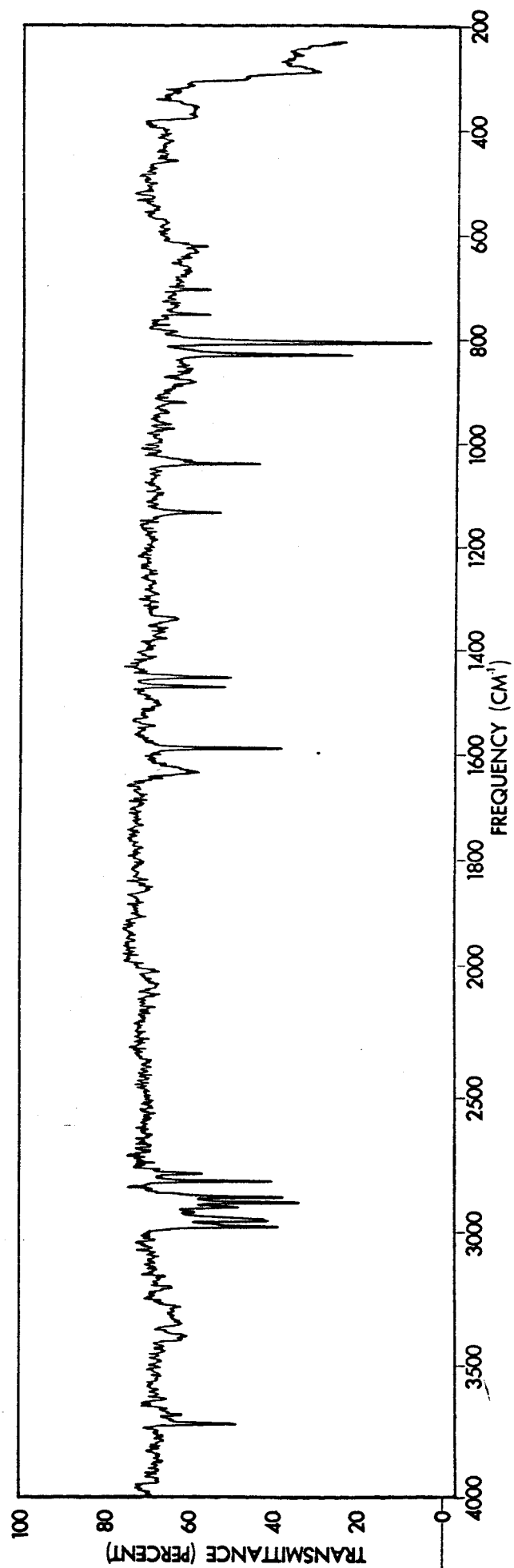
slower rates of 20 to 30 μM per minute which cannot be achieved with our present cryogenics apparatus; however, we are now in the process of modifying this apparatus in order to allow longer running times thus slower deposition rates. Due to the high cost of the deuterated samples of methylamine, it is necessary to work out all the experimental difficulties before attempting to record their spectra.

We have recorded the matrix spectrum of CH_3NH_2 in 1:3000 and 1:450 mole ratios with Ar as the matrix gas and in 1:200, 1:300, 1:450, 1:600, and 1:900 mole ratios with N_2 as the matrix gas. All samples were deposited in an Air Products Cryostat maintained at liquid hydrogen temperatures and the spectra recorded between 250 and 4000 cm^{-1} using a Perkin Elmer Model 521 Spectrophotometer. Sample spectra are enclosed (See Figures 1-3) and the observed frequencies along with tentative assignments are shown in Table I.



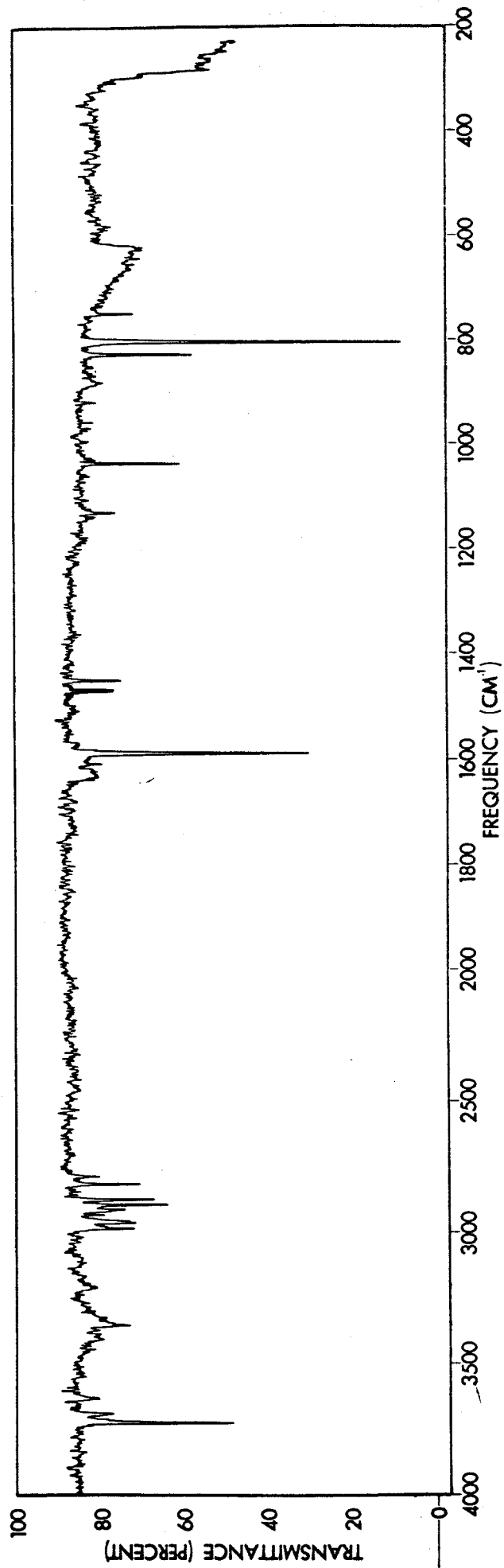
Infrared Spectrum of Matrix Isolated CH_3NH_2

$\text{N}_2:\text{CH}_3\text{NH}_2=200:1$



Infrared Spectrum of Matrix Isolated CH_3NH_2

$\text{N}_2:\text{CH}_3\text{NH}_2=450:1$



Infrared Spectrum of Matrix Isolated CH_3NH_2

$\text{N}_2 : \text{CH}_3\text{NH}_2 = 900:1$

Table I

Infrared Spectrum of Matrix Isolated $\text{CH}_3\text{NH}_2(\text{N}_2:\text{CH}_3\text{NH}_2-450:1)^*$

Band Centers (cm^{-1})	Relative Intensity	Tentative Assignments
3725	S	H_2O stretching mode
3690 (sh)	W	
3390 (bd)	W	ν_1 and $\nu_{10}-\text{NH}_2$ stretching modes and possibly first overtone of ν_4
3343 (bd)	W	
3280 (bd)	W	
2986	S	
2978 (sh)	W	
2964	S	
2958	S	ν_2, ν_3 and $\nu_{11}-\text{CH}_3$ stretching modes coupled in Fermi resonance with ν_5 and ν_6
2950 (sh)	M	
2933	M	
2928	M	
2913	M	
2895	S	
2874	S	
2816	S	
2787	M	
1645 (bd)	M	$\nu_4-\text{NH}_2$ deformation
1600	S	H_2O -bending mode
1483	MS	ν_5 and $\nu_6-\text{CH}_3$ symmetric deformations
1464	MS	

Table I (continued)

Infrared Spectrum of Matrix Isolated $\text{CH}_3\text{NH}_2(\text{N}_2:\text{CH}_3\text{NH}_2-450:1)^*$

Band Centers (cm^{-1})	Relative Intensity	Tentative Assignments
1340 (bd)	W	polymer band
1144	MS	ν_7 - CH_3 wagging mode
1050	MS	ν_8 -C-N stretching mode
841	S	
816	VS	ν_9 - NH_2 wagging mode
793	W	
715	W	
388	VW	
374	VW	
300	S	ν_{15} - NH_2 torsion

Abbreviations: M, medium; S, strong; W, weak; MS, medium strong; VS, very strong
VW, very weak; sh, shoulder; bd, broad.

*Band Centers listed in this table are taken from the 450:1; $\text{N}_2:\text{CH}_3\text{NH}_2$ spectrum and are obviously not those observed for the 200:1 and 900:1 mole ratios in all cases.

The NH_2 stretching vibrations in the 3300 cm^{-1} region are very weak as expected (N-H stretching vibrations are usually weak). However, the contour of these bands clearly points to the probability that there is still an appreciable amount of N---H-N type hydrogen bonding even at mole ratios as high as 1:900. It is doubtful that we shall be able to eliminate this complicating feature, but it is of relatively little importance to a correct assignment of the matrix spectrum. In the 2900 cm^{-1} region, one expects to find three C-H stretching vibrations, and there are twelve bands observed in this region. Lord and Gray,¹ after observing unusually complicated gas phase structure in this region, pointed out the probability that this region was complicated by Fermi resonance of the $-\text{CH}_3$ deformation overtones with the $-\text{CH}_3$ stretching fundamentals. Our matrix spectrum very clearly shows that this is indeed the case.

The CH_3 and NH_2 deformational region is quite readily assigned. We assign the N-H deformation to the relatively broad band at 1645 cm^{-1} . Again the broadness of this band is evidence of N---H-N hydrogen bonding. The strong sharp absorption at 1600 cm^{-1} arises from the H_2O bending mode of the water impurity. The characteristic H_2O stretching mode is also seen at 3725 cm^{-1} . The two symmetric CH_3 deformations are assigned to the bands at 1464 and 1483 cm^{-1} . We do not observe any other bands in this region

which could be assigned to the antisymmetric CH_3 deformation of species A'' . A similar result was also concluded by Lord and Gray. The A'' CH_3 wagging and the C-N stretching modes ν_7 and ν_8 are also quite readily assigned respectively to the bands at 1140 and 1050 cm^{-1} . The (A'') CH_3 wagging mode ν_{14} is not observed.

Lord and Gray¹ have assigned the $-\text{NH}_2$ wagging mode for CH_3NH_2 at 780 cm^{-1} . They stated that this band had a strong central Q branch and rather complicated structure in the R and P branches and was therefore probably a hybrid band. In all of our $\text{CH}_3\text{NH}_2:\text{N}_2$ matrix spectra we find two strong bands at 816 and 841 cm^{-1} . As stated before, these two bands shift to 790 and 797 cm^{-1} with a reversal in their relative intensity in an Argon matrix.

A first thought would be to rationalize these two bands by considering inversion doubling. They are split by a reasonable amount, but their intensities are far from being equal as one would expect for inversion doubling. Also, Pimentel *et al.*,⁵ have shown that the inversion doubling in ammonia is quenched in a N_2 -matrix at 20°K. There is no evidence which would lead us to believe that it would not also be quenched in CH_3NH_2 under the same conditions. Another possibility is that the missing NH_2 twisting vibration of symmetry species A'' is represented by one of these bands. The intensity of even the weaker of these two bands provides strong evidence against the above assumption. A third possibility is that the weaker of the two bands arises from some dimeric or polymeric species in the matrix but we have no

conclusive evidence to confirm this assumption at present. Rather than speculate further on the assignment of these bands, we feel that the additional data from the matrix spectra of CD_3NH_2 and CD_3ND_2 will provide the necessary information need to correctly interpret the results and this interpretation will be given in the next progress report.

We have no explanation as yet for the two weak bands at 715 and 763 cm^{-1} . The strong band at about 300 cm^{-1} has been tentatively assigned as the tortional oscillation. Lord and Gray¹ calculated this band to be 264 cm^{-1} and Hadni⁶ supposedly observed an absorption maximum at 269.5 cm^{-1} . However, it is reasonable that the N_2 -cage would restrict this oscillation producing a higher internal rotational barrier, thus causing a larger splitting between energy levels.

Solid Phase Spectra of CH_3NH_2 , CD_3NH_2 , CD_3ND_2

Solid phase spectra of CH_3NH_2 , CD_3NH_2 , and CD_3ND_2 have been recorded at liquid nitrogen temperature using a cold cell similar to that of Wagner and Hornig.⁷ All spectra were recorded on a Perkin-Elmer 521 Spectrophotometer. Table II lists the observed frequencies with tentative assignments. The data will be used to supplement the matrix phase spectra and aid in making correct assignments for these molecules. A more complete interpretation of the data will be given in the next technical report.

Table II Tentative Solid Phase Assignments

Approximate Description	Vibration No.	$\text{CH}_3\text{NH}_2(\text{cm}^{-1})$ Intensity	$\text{CD}_3\text{NH}_2(\text{cm}^{-1})$ Intensity	$\text{CD}_3\text{ND}_2(\text{cm}^{-1})$ Intensity
NH_2 Stretching Vibrations	$\nu_1(\text{A}'), \nu_{10}(\text{A}'')$	3330		2485 (db) S
		3322	S	2479 S
		3260	S	2445 M
			M	2415 M
CH_3 stretching Vibrations	$\nu_2(\text{A}'), \nu_3(\text{A}'), \nu_{11}(\text{A}'')$	3191	S	2370 (sh) MS
		2963		2304 S
		2942	S	2330 (sh) MS
		2918	MS	2241 (sh) MW
		2899	S	2220 S
		2881	S	2190 S
		2865	S	2141 MW
		2808	M	2105 MW
		2793	MS	2061 S
		1612	S	2050 (sh) MS
NH_2 Deformation CH_3 Deformation	$\nu_4(\text{A}')$ $\nu_{12}(\text{A}'')$	1460	MW	2028 (sh) MW
		1472	M	1205 S
CH_3 Deformations	$\nu_5(\text{A}'), \nu_6(\text{A}')$			1057 MW
				1121 MS
				1110 (sh) M
CH_3 Wagging Vibrations	$\nu_7(\text{A}')$ $\nu_{14}(\text{A}'')$	1448	M	1070 MS
		1171 (sh)		
		1161	MW	
			M	
		826	MW	730 S
		815	M	710 S
		801		683 S

Table II (Continued)

Approximate Description	Vibration No.	$\text{CH}_3\text{NH}_2(\text{cm}^{-1})$ Intensity	$\text{CD}_3\text{NH}_2(\text{cm}^{-1})$ Intensity	$\text{CD}_3\text{ND}_2(\text{cm}^{-1})$ Intensity
C-N Stretching Vibration	$\nu_8(\text{A}')$	951	S	939
NH ₂ Wagging Vibration	$\nu_9(\text{A}')$	909	S	722 (sh)
NH ₂ Twisting Vibration	$\nu_{13}(\text{A}'')$			
Tortion	$\nu_{15}(\text{A}'')$	498	S	358

Abbreviations: S, strong; M, medium; W, weak; MS, medium strong; ~~MM~~, medium weak; sh, shoulder; db, doublet

Future Work

With the cryostat set up for continuous operation for periods of twenty or thirty hours the matrix spectra of CD_3ND_2 and CD_3NH_2 will be recorded. Interpretation of the observed bands will be given and it is hoped that a rough draft of a paper will be ready by the next reporting date. Matrix isolation spectrum of N_2D_4 will be studied and analysis of the results will be attempted. Work on other molecules which could possibly be constituents of the Jovian atmospheres will be initiated if time permits.

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